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(54) Title: ENERGY CURABLE ADDUCT CONTAINING A SILANE GROUP AND COATINGS THEREFROM

(57) Abstract: Disclosed is a polyfunctional liquid polyurethane-containing adduct wherein the adduct contains statistically as a first functional group at least one structo-terminal polymerizable group and at least one second structo-terminal functional group per molecule which is a silane moiety. Such compounds are useful in radiation curable coatings.

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on total weight of the composition; and in a second step, exposing said treated surface to an energy source that can induce polymerization of the composition.

In a fourth aspect, this invention is to an article which comprises a substrate that has adhered to one of its surfaces a polymeric film wherein said article is obtained by  
5 the process as above mentioned.

The silane adducts of the present invention give improved compatibility of silane agents in energy cured formulations. Such crosslinkable adducts have a reduced tendency of component separation in energy-curable formulations and therefore reduced migration issues. The reduced migration, particularly of the silane, is a result  
10 of the silane and polymerizable groups being linked to one molecule and once a functional group is polymerized into the polymer matrix, the other functional group is also fixed. Formulations using the present adducts are also useful for reducing the surface free energy of coating formulations and improving adhesion to substrates, especially inorganic substrates such as metal and glass. The adducts also provide  
15 techniques for dual cure crosslinking of energy cured systems (moisture cure of silane groups in addition to energy cure) giving three dimensional polymer inter-connectivity, leading to higher overall crosslink density.

The adduct of this invention is characterized in that it is a polyfunctional liquid polyurethane adduct bearing energy polymerizable groups and a second different  
20 functional group which is a silane moiety. By the term "liquid" it is meant that the adduct has a pour point of 50°C or less, and preferably is a liquid at a temperature of from 0°C to 40°C.

The polyfunctional liquid polyurethane-containing adduct has a polyol core which is extended with an isocyanate moiety and terminated with at least two functional  
25 groups. These functional groups are structo-terminal, that is, they are not pendent, that is, not hanging or branching from the backbone. Statistically, within the same adduct molecule, at least one chain end bears a polymerizable group, and at least one chain end bears a silane group.

By the term "polymerizable group" it is understood a moiety that is susceptible  
30 to polymerization when exposed to an energy source, optionally in the presence of an

7 energy polymerizable moieties per molecule and from 7 to 1 silane moieties are present, and in the case of 2 end groups per molecule, statistically 1 energy polymerizable moiety and 1 silane moiety are present. The optimum ratio of polymerizable moieties to silane moieties will depend on the intended purpose and surface to be coated and can vary within the ranges of from 1:7 to 7:1, and preferably from 1:2 to 2:1.

By chain ends implies the silane moieties will be structo-terminal. For a polyol having a functionality of 2, this can be represented by



10  $X^1$  represents the divalent radical formed between an isocyanate and the isocyanate reactive moiety of the polyol;

where  $X^2$  represents the divalent radical formed between an isocyanate and the isocyanate reactive moiety of  $G-R^2SiY^1Y^2Y^3$  or the isocyanate reactive moiety of a polymerizable compound;

15 ISO represents a moiety derived from a polyisocyanate component having 2 isocyanate reactive groups;

POLYOL represents a moiety derived from a polyol component comprising a compound having 2 isocyanate reactive functional group, such a polyol can have more than 2 isocyanate reactive functional groups as described herein;

20 Z represents a moiety derived from  $G-R^2SiY^1Y^2Y^3$  having at least one isocyanate reactive groups or a polymerizable group, where  $G-R^2SiY^1Y^2Y^3$  is as defined above.

The polyfunctional liquid polyurethanes adducts of the present invention can contain additional functional moieties such as an aryl, alkyl, ester, nitrile, alkene, alkyne, halogen, silyl or combinations thereof. The equivalents of polymerizable and silane moieties and optionally additional functional groups is such that the adduct is substantially free of any isocyanate functionality or any isocyanate-reactive functionality.

30 The adducts of the invention are prepared by reaction of an isocyanate-terminated prepolymer with substances containing the polymerizable group and with substances containing the silane moiety. An isocyanate-terminated prepolymer is

carbonate polyols, polyolefinic polyols and polyphosphate-based polyols. Such polyols are known in the art.

The polyol generally has an equivalent weight of from 100 to 5000. Preferably the polyol has an equivalent weight of from 200 or greater, more preferably from 300 or greater. Preferably the equivalent weight is less than 3000, more preferably less than 2000, and yet more preferably less than 1500. Preferably the polyol is a polyester or polyether polyol. Highly preferred are polyoxyalkylene polyols where the oxyalkylene entity comprises oxyethylene, oxypropylene, oxybutylene or mixtures of two or more thereof. Especially preferred are oxypropylene or oxyethylene or mixtures thereof. More especially preferred is oxypropylene. Processes for making such polyols are known to those in the art.

Suitable polyoxyalkylene polyols are exemplified by various commercially available polyols as used in polyurethane, lubricant, surfactancy applications and include polyoxypropylene glycols designated as VORANOL™ P-2000 and P-4000 with respectively equivalent weights of 1000 and 2000; polyoxypropylene-oxyethylene glycols such as DOWFAX™ DM-30 understood to have an equivalent weight of 300 and an oxyethylene content of 65 weight percent, and SYNALOX™ 25D-700 understood to have an equivalent weight of 2750 and an oxyethylene content of 65 weight percent, all available from The Dow Chemical Company; polyoxyethylene triols available under the trademark TERRALOX™ and designated as product WG-98 and WG-116 understood to have a molecular weight of 700 and 980, respectively, polyoxypropylene-oxyethylene triols designated as VORANOL™ CP 1000 and CP 3055 understood to have respectively a molecular weight of 1000 and 3000, and VORANOL™ CP 3001 understood to have a molecular weight of 3000 and an oxyethylene content of 10 weight percent and VORANOL™ CP 6001 understood to have a molecular weight of 6000 and an oxyethylene content of 15 weight percent, all available from The Dow Chemical Company; poly(oxypropylene-oxyethylene) hexols including VORALUX™ HF 505 understood to have a molecular weight of 12000, and polyoxyethylene hexols including TERRALOX™ HP-400 understood to have a molecular weight of 975, both available from The Dow Chemical Company; higher functionality polyether polyols including those based on carbohydrate initiators such as,

weight percent. Measured isocyanate contents may be higher depending on residual content of unreacted polyisocyanate.

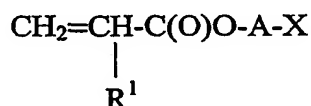
The so obtained isocyanate-terminated prepolymer is reacted with isocyanate-reactive substances containing the polymerizable group and with isocyanate-reactive substances containing the silane moiety.

Isocyanate-reactive substances containing the silane moiety are described above.

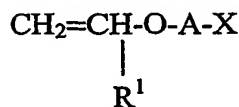
Isocyanate-reactive substances containing the polymerizable moiety are substances which contain a functional group that can polymerize under the influence of an energy source and which additionally contain a functional group that can react with an isocyanate such as described above. The isocyanate reactive substance could also be an isocyanate if it is the intention to couple to the prepolymer by formation of an isocyanurate or carbodiimide linkage.

One type of radiation polymerizable functionality is ethylenic unsaturation which in general is polymerized through radical polymerization such as can be initiated through exposure to actinic radiation, but can also be polymerized through cationic or anionic polymerization. Examples of ethylenic unsaturation are groups containing vinyl ether, vinyl ester (for example, acrylate or methacrylate) or acrylamide functionality. Preferably, the polymerizable group is a vinyl ester group or a vinyl ether group. Most preferably, the polymerizable group is an acrylate or methacrylate group.

The polymerizable vinyl ester can be represented by the following formula:



and the vinyl ether can be represented by the formula



where X is an isocyanate-reactive functional group, such as -OH, -SH, -COOH

or

-NHR where R is as previously defined;  $\text{R}^1$  is a substituent comprising hydrogen, a C1 to C3 alkyl or acyl radical or a halogen or other group which will not deleteriously affect the curing of the finished adduct, and A is an aliphatic or aromatic hydrocarbon

the desired content of moieties. This reaction is generally conducted in a sequential manner with the isocyanate-reactive material containing the polymerizable moiety being first reacted with the prepolymer and then in a subsequent step the isocyanate-reactive silane containing compound is introduced. When the isocyanate-reactive substance contains a secondary amine, as with some of the silane compounds described above, it is necessary that the isocyanate reactive silane-containing moiety is first reacted with the prepolymer and then in a subsequent step the isocyanate-reactive substance containing the polymerizable moiety is introduced. Such a sequence of steps aids in avoiding reaction of an acrylate with the secondary aminosilanes by the Michael addition reaction, resulting in oligomers and eventually gelation.

When capping the isocyanate-terminated prepolymer with the isocyanate reactive substances it may be desirable to control the viscosity of the reactants, process or final adduct. This can be achieved by introducing a "reactive diluent" to the process. Such diluent can be introduced at any stage of the process. By the term "reactive diluent" it is understood a liquid substance which is able to undergo polymerization when exposed to the previously mentioned energy sources yet does not undergo reaction with the isocyanate-terminated prepolymer nor with the isocyanate-reactive substances. Exemplary of suitable reactive diluents are compounds comprising acrylate or methacrylate functionality and those characterized by absence of an isocyanate-reactive functionality. Preferred diluents include isoboranolacrylate (IBOA), tripropyleneglycoldiacrylate (TPGDA), N-vinyl pyrrolidone, isopropylacetate and dipropyleneglycoldiacrylate (DPGDA).

Preferably the amount of reactive diluent added is sufficient to give a viscosity of the final adduct solution of between 500 to 2,000 cps. HEMA may also be used as a reactive diluent. When HEMA is used, it is intuitively obvious that HEMA can not be used as a reactive diluent until after partial capping of the -NCO groups with the silane-containing moiety. After such capping, HEMA is then added at an excess so that all the remaining -NCO groups are capped and there is remaining unreacted HEMA to act as a diluent.

For addition of a functional group to the isocyanate-terminated prepolymer, the process temperature is chosen for convenience of reaction time and can be greater than

sequentially, in either order, leading to an increased crosslink density, compared to materials with only energy cure mechanisms. This allow coatings where it is desired to increase hardness, solvent resistance and abrasion resistance of the coating.

It is of critical importance to avoid adding raw materials which have high residual acidity levels to formulations containing adducts of the present invention, for example, acrylic acid residues normally found in standard epoxy or polyether acrylates that have been produced by direct acrylation. The reason for this is that silane groups reaction is catalyzed by acidic groups. If this reaction occurs too soon, the formulation can have a short pot life and result in solidification or viscosity increase prior to use as a coating application..

The adducts of this invention have principle utility as a coating or additive to a coating formulation to coat substrates such as plastic, metal, natural textiles, synthetic textiles, minerals including glass and wood and wood products including paper where it is desirable to obtain adhesion to a surface.

The invention defined above will now be illustrated with reference to the following Examples.

#### EXAMPLE I

##### Preparation of prepolymer

To a 2-liter glass reactor was added 798.2 grams of toluene diisocyanate (TDI) (VORANATE™ T-80, VORANATE is a trademark of The Dow Chemical Company) and 0.22 grams of benzoyl chloride. The mixture, under nitrogen, was heated to a stable temperature of 50°C and then 690.1 grams of a 6-functional , 303 equivalent weight EO/PO polyol, 5.6 percent by weight OH, was added at a rate of 10 g/min. Digestion of the reaction mixture continued for 4 hours. After digestion the product was recovered. The recovered material was subjected to a short-path distillation under less than 0.05 mbar, 160°C top, 70°C bottom. The recovered isocyanate-terminated stripped prepolymer had a free TDI content of <0.1 weight percent and a measured NCO content of 8.6 weight percent.

Table 1: UV formulation composition

	Sample A (from Example 1)	50pbw
5	Teactive polymer T2011.01	20pbw
	TPGDA	26pbw
	Photoinitiator Irgacure* 184	2 pbw
	Photoinitiator Darocure 1173	2 pbw
10	*Irgacure and Darocure are Trademarks of Ciba Speciality Chemicals.	

Coating Sample Testing methods.

## 1. Cross-Hatch Adhesion test.

15           Adhesion to a metal surface was measured using ASTM D 3359-97 "Standard Test Methods for Measuring Adhesion by Tape Test". An Erichsen Model 295 manual cross hatch cutter was used to produce the crosshatch pattern in the coatings. Coating thickness was 50 microns. Permacel 99 tape was used to adhere to the crosshatch pattern. The tape was rubbed down well onto the coating using medium pressure from the index finger. The tape was allowed to remain in contact with the coating for 1 minute. The tape was then peeled back at 180° angle from the coated substrate at a rapid constant rate. The amount of coating removed was judged and recorded. The test method then groups the percentage removal into 6 classes, as follows:

- 25   5B    0% removed, that is 100% adhesion, no coating removed  
      4B    less than 5% removed  
      3B    5-15% removed  
      2B    15-35% removed  
      1B    35-65% removed  
  30   0B    More than 65% removed

These groups 5B through 0B are recorded as the result.

## 35   2. Pendulum Hardness



should take one second and is counted as 1 double rub. The coating surface is observed during the test. At the first sign of failure (cracking, swelling, delamination) the test is stopped and the number of double rubs required for failure is recorded.

## 5. Dynamic mechanical Spectroscopy (DMS)

A Rheometrics Solids Analyser RSA II was used on 100-200 micron coating films to obtain DMS plots. Samples were heated from  $-100^{\circ}\text{C}$  to  $150^{\circ}\text{C}$  at  $5^{\circ}\text{C}/\text{min}$  heating rate in the test chamber, held in place using thin film tension mode fixture. A strain of 0.1 was utilized with a frequency of 1 Hz (6.28 rad/s).

## Results

As designed the formulation presented in Table 1 should have a dual cure mechanism. That is, the terminal acrylate groups within the resin are polymerised on exposure to the UV source to convert the wet coating to a dry film. A second reaction takes place over time, involving the silane groups of the Sample A resin. Thus the testing of the dry film coated Q-Panels was repeated over a period of 1 week. The data in Table 2 indicates the test results 1 day after UV exposure and 1 week after exposure.

Table 2: Dry coat test results:

Property	1 Day old	1 week old
Tg by DMS	$48^{\circ}\text{C}$	$75^{\circ}\text{C}$
Konig Hardness	35 sec	115 sec
Adhesion on QD-46 steel panel	0B (20%)	5B (100%)
Adhesion on glass panel	0B (20%)	5B(100%)
Acetone double rubs	>50	>50
Reverse Impact	>100cm	>100cm

Clearly evident is the desired property of improved adhesion performance to both steel and glass panels. As expected, the glass transition temperature increases with time as the second silane reaction takes place. This also results in an improved hardness performance of the coating.

## WHAT IS CLAIMED IS:

1. A liquid polyurethane-containing adduct wherein the adduct contains as a first functional group at least one structo-terminal polymerizable group and at least one second structo-terminal functional group per molecule which is a silane moiety.
- 5        2. The adduct of Claim 1 wherein the adduct is derived from an NCO-terminated prepolymer containing less than 1 percent by weight of free isocyanate monomer.
3. The adduct of Claim 1 wherein the adduct has 2 to 8 structo-terminal groups.
- 10       4. The adduct of Claim 1 wherein the polymerizable group is selected from, vinyl ester, vinyl ether or acrylamide functionality.
5. The adduct of Claim 4 wherein the polymerizable group is selected from acrylate or methacrylate.
6. The adduct of Claim 1 wherein the molar ratio of polymerizable functional  
15 groups to silane moieties is 2:1 to 1:2.
7. An energy curable formulation for coating a substrate, wherein the formulation contains from 1 to 99 percent by weight of the adduct of any one of Claims 1 to 6.
8. A process of coating a substrate surface comprising applying to the surface  
20 of a substrate a formulation of Claim 7 and in a subsequent step, exposing the treated surface to an energy source to induce polymerization of the formulation.
9. The process of Claim 8 wherein the energy source is actinic radiation, ultraviolet radiation, electron-beam radiation or thermal radiation.
10. An article prepared by the process of Claim 9.
- 25       11. A method for making an adduct containing at least one structo-terminal polymerizable group and at least one structo-terminal silane group comprising the steps of  
  - (1) mixing a polyol containing isocyanate reactive groups with a polyisocyanate at a stoichiometric excess of isocyanate groups to isocyanate groups to form an  
30 isocyanate terminated prepolymer;

## INTERNATIONAL SEARCH REPORT

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## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09D175/16 C08G18/10 C08G18/28 C08G18/67

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 850 961 A (LUCENT TECHNOLOGIES INC) 1 July 1998 (1998-07-01) page 3, line 57 -page 4, line 9; claims 1,4; examples 2,3	1-14
X	EP 0 851 246 A (LUCENT TECHNOLOGIES INC) 1 July 1998 (1998-07-01) examples 2,3	1-14
X	WO 97 14737 A (JAPAN SYNTHETIC RUBBER CO LTD ;KOMIYA ZEN (JP); UKACHI TAKASHI (JP) 24 April 1997 (1997-04-24) page 23, line 25 -page 24, line 6 page 27, line 33 -page 28, line 3 -/--	1-14

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
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Patent document cited in search report		Publication date		Patent family member(s)	Publication date
EP 0850961	A	01-07-1998	US	6355751 B1	12-03-2002
			EP	0850961 A1	01-07-1998
			JP	3278111 B2	30-04-2002
			JP	11035847 A	09-02-1999
EP 0851246	A	01-07-1998	US	5822489 A	13-10-1998
			EP	0851246 A1	01-07-1998
			JP	3207145 B2	10-09-2001
			JP	10197731 A	31-07-1998
WO 9714737	A	24-04-1997	JP	9110947 A	28-04-1997
			AU	7229096 A	07-05-1997
			WO	9714737 A1	24-04-1997
WO 9611217	A	18-04-1996	JP	8109229 A	30-04-1996
			AU	700684 B2	14-01-1999
			AU	3755495 A	02-05-1996
			CA	2202253 A1	18-04-1996
			DE	69506577 D1	21-01-1999
			DE	69506577 T2	29-07-1999
			DK	785959 T3	16-08-1999
			EP	0785959 A1	30-07-1997
			WO	9611217 A1	18-04-1996
			US	6191187 B1	20-02-2001